The Growth of Colloidal Gold Particles Formed by the Bredig Method in Aqueous Solutions of Barium Chloride

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DISSERTATION

Submited in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science in Columbia University.

BY

LEO WENDELL BRIGGS, B.A., M.A.

NEW YORK CITY

1923

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To My

Father and Mother

ACKNOWLEDGMENT

The author wishes to express to Professor H. T. Beans his sincere thanks for the suggestion of the problem and for his generous assistance and advice throughout the course of the investigation.

He also wishes to thank the other members of the Chemistry Department for their co-operation and assistance.

THE GROWTH OF COLLOIDAL GOLD PARTICLES BY THE BREDIG METHOD IN DILUTE AQUEOUS SOLUTIONS OF $BaCl_2$

The fact that the presence of a small concentration of electrolyte is required in the formation of a stable colloidal gold hydrosol, by the Bredig method may now be considered as thoroughly established.[1] Beans and Eastlack[2] have shown qualitatively the range of concentrations of various electrolytes necessary for the production of these stable sols. They have further pointed out that there is a relation between the stabilizing effect and the ability of the ion to form a stable compound with gold.

Beaver[3] has shown that the amount of electrolyte necessary to stabilize Bredig gold sols is roughly proportional to the amount of colloidal gold present. This is true for the sols with which he worked, although not true for the entire range of concentrations. Precipitating the gold of these hydrosols by two methods (i. e., freezing and centrifuging) he was able to obtain strong evidence of an association of the ions of the electrolyte with the gold particles of these hydrosols in a "complex" and to show that it is the negative ion which is the active constituent in stabilizing the gold of the sols, although both ions are absorbed in this "complex."

Miller[4] has considered the relationship between concentration of electrolyte and the amount of stable gold in the sol. He found that for each concentration of an electrolyte there is a maximum amount of gold which can be stabilized. He also found that these maximum concentrations of gold vary for different concentrations of electrolyte passing through one or more maxima, when plotted against increasing concentration of electrolyte.

It is the object of this work to study in greater detail these and certain other factors influencing the formation of these colloidal gold particles.

APPARATUS AND MATERIALS

All solutions were made up in water having a specific conductivity of 1 to 1.3×10^{-6} mhos. The hydrochloric acid was Baker and Adamson's C.P. acid. The barium chloride was crystallized three times from conductivity water and the final product showed no spectroscopic impurities. A standard solution was made up containing 4.848 gms. of $BaCl_2$ per liter. Because of the fact that very dilute solutions of barium chloride were used, .0005 N. solutions were made up and these in turn were diluted in making the desired solutions.

The gold wire and arcing apparatus were the same as used by Beans and Eastlack with the addition of a motor-driven stirrer, ammeter and voltmeter. The voltmeter was connected to measure the potential difference between the electrodes. The arcing stand was improved, making it possible to obtain a continuous arc. The time of arcing was measured with a stop watch.

The centrifuge was a "type three centrifuge" of the International Equipment Company, with rotating arms two feet in diameter and a speed of approximately 2000 revolutions per minute. This gives a force of 1200 times gravity.

The burettes, pipettes, volumetric flasks and set of weights were standardized by the usual methods.

METHOD OF PROCEDURE

The solution of barium chloride, 250 cc of a given concentration, was placed in a 400 cc pyrex beaker and surrounded by an ice bath. The glass stirrer, gold electrodes, and thermometer were inserted through holes in a cover, placed over the beaker, and adjusted beneath the surface of the solution. A continuous arc, of constant current and potential difference between the electrodes, was maintained, by frequent adjustment, for two minutes or until the temperature of the solution had reached 22°C. The circuit was then broken and the temperature allowed to fall to 16°C. This alternate arcing and cooling with continuous stirring was continued until the desired total time of arcing had been

reached. The solution was then divided into five samples, placed in pyrex tubes and centrifuged at 1200 times gravity. These samples were removed at intervals and dummy loads put in their places. Thus the speed of the centrifuge remained unaltered throughout the run. Twenty-five cc of the solution from each sample were siphoned off without disturbing the precipitated gold in the bottom of the tubes. The gold in this volume of the solution was precipitated by adding a drop of conc. HCl, filtered from solution, ignited, cooled in a desiccator and weighed.

The beaker and glass centrifuge tubes were well steamed before each run was made. These tubes were stoppered to exclude any dust or foreign material from the samples. Special care was taken to keep all conditions uniform and constant. The stirrer was set at the same speed each day, and the speed of the stirrer frequently checked. The electrodes were placed at the same depth in the solution each time and, due to the fact that the stirrer and electrodes were inserted through holes in the cover, they were placed, each time, in the same position relative to each other. Since it is not the actual temperature of the solution but the difference between the high temperature of the arc and that of this surrounding medium that is important,[5] a variation of six degrees in the temperature of the solution is negligible and the temperature may be regarded as constant. The temperature was low enough and the electrodes placed deep enough in the solution to prevent much evaporation of water from the solution.

Although the potential difference between the input terminals was variable, it was possible, by adjustments of the distance apart of the electrodes (that is, the resistance between the electrodes) and the slide wire resistance in series with the arc, in respect to each other, to hold the current constant at $3.3 \pm .1$ amperes and the difference in potential across the arc at 28.5 ± 1.5 volts. Slight variations in the speed of the centrifuge due to fluctuations in the voltage could not be avoided. However, with the same load at all times, it was assumed that the small variations compensated each other and that the speed was in effect constant.

Thus the following factors may be regarded as constant:

Temperature—19°±3°C.

Potential Difference—28.5±1.5 volts.

Current—3.3±.1 ampere.

Velocity of Centrifuge—2000 r.p.m.

Rate of Stirring.

The factors which have been studied as variable quantities are:

Concentration of gold in solution.

Concentration of electrolyte in solution.

Time of arcing.

Time of centrifuging.

Thus 250 cc of .00005 N barium chloride solution have been arced twenty-five minutes, with constant rate of stirring, constant temperature, current, and potential difference as set forth above. This sol was then divided into five parts and these parts centrifuged ½, 1, 2, 4, and 6 hours, respectively. After centrifuging, the gold remaining in twenty-five cc of each was precipitated (by adding a drop of conc. HCl), filtered from the solution, ignited, cooled in a desiccator, and weighed. This was repeated for 31, 37, etc., minutes of arcing and again the whole process repeated for .00013, .00021 and .00029 N solutions of barium chloride. The results in milligrams per twenty-five cc are recorded in Tables I to V, inclusive.

TABLE I

.00005 N $BaCl_2$

Time of arcing in 250 cc (in min.)	Gold (in mgs.) remaining in 25 cc solution after centrifuging				
	30 min.	1 hour	2 hours	4 hours	6 hours
25	9.1	7.6	6.5	5.6	5.3
31	10.2	8.7	7.1	5.6	5.2
37	13.0	11.2	10.1[1]	7.9[2]	6.9[3]
43	13.1	10.5	9.2[1]	7.4[2]	6.2[3]
49	12.5	10.0	7.2	4.8	3.8
55	10.5	7.4	4.7	3.6	2.6
61	8.3	4.9	2.8	1.7	1.4

[1] Centrifuged 1 hour 30 minutes.
[2] Centrifuged 2 hours 30 minutes.
[3] Centrifuged 4 hours 30 minutes.

TABLE II

.00013 N $BaCl_2$

Time of arcing in 250 cc (in min.)	Gold (in mgs.) remaining in 25 cc solution after centrifuging				
	30 min.	1 hour	2 hours	4 hours	6 hours
25	10.7	9.4	8.2	7.5	6.2
37	13.8	11.9	9.6[1]	8.3	7.7
49	16.5	14.7	11.9[2]	9.9[3]	8.8
61	19.5	16.4	13.5	11.1	10.5
73	21.9	18.3	14.0	10.0	9.1
85	18.9	14.0	10.3	7.8	7.1

[1] Centrifuged 2 hours 10 minutes.
[2] Centrifuged 2 hours 5 minutes.
[3] Centrifuged 3 hours 55 minutes.

TABLE III

.00021 N $BaCl_2$

Time of arcing in 250 cc (in min.)	Gold (in mgs.) remaining in 25 cc solution after centrifuging				
	30 min.	1 hour	2 hours	4 hours	6 hours
25	8.6	7.7	6.4	5.0	4.0
37	13.7	12.2	9.3	6.9	5.8
49	15.8	12.9	10.2	6.8	5.4
73	19.7	14.7	10.2	7.1	5.2
97	23.7	18.6	11.3	6.3	4.1
121	22.8	17.3	10.5	6.7	6.2
145	15.9	11.4	7.4	5.5	3.3

TABLE IV

.00029 N $BaCl_2$

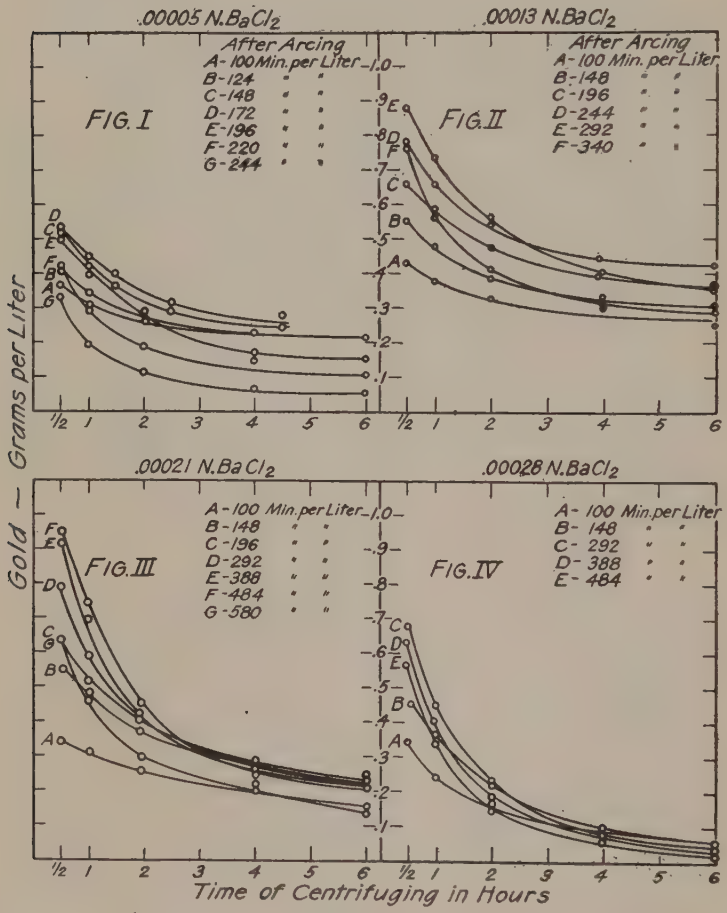
Time of arcing in 250 cc (in min.)	Gold (in mgs.) remaining in 25 cc solution after centrifuging				
	30 min.	1 hour	2 hours	4 hours	6 hours
25	8.6	6.1	4.1	2.5	1.4
37	11.7[1]	9.0	5.5	2.4	1.4
73	16.9	11.2	5.7	2.0	1.2
97	15.7	10.0	4.6	1.9	.9
121	14.2	8.4	3.7	1.4	.4

[1] Centrifuged 33 minutes.

TABLE V

.00037 N $BaCl_2$

Time of arcing in 250 cc (in min.)	Gold (in mgs.) remaining in 25 cc solution after centrifuging				
	30 min.	1 hour	2 hours	4 hours	6 hours
25	5.4	2.8	1.0	None	None
37	6.1	2.5	.9	None	None



These results are shown graphically in Figures I to IV, inclusive. Since arcing in 250 cc of solution gives exactly the same result as arcing in a liter (with same concentration of electrolyte) four times as long, the actual results multiplied by four have been plotted, and recorded as time of arcing per liter of solution. Also the number of milligrams per twenty-five cc has been multiplied by forty and plotted as grams of gold per liter.

Several opinions have been expressed as to the exact process whereby the gold passes into the colloidal state. Ostwald[6] holds that the process is of an electrochemical nature and that the substance goes into the liquid in atomic form under electric forces and afterwards becomes aggregated. Benedicks[7] and others lay stress on the thermal side of the process and are of the opinion that the metal partly volatilizes and partly melts.

It is certain that a small space around the heated electrodes contains only water vapor. Any process in which the atoms leave the electrodes individually or a few at a time may be compared to evaporation. If pure water is used the gold does not pass into the colloidal state, but is thrown down as a blackish violet powder. Let us assume that these atoms of gold, distilled from the electrode, strike the wall of liquid surrounding the electrodes. If a very small number of electrolyte molecules is present in the water, very small particles of gold are formed, and these are extremely stable, their stability approaching that of ions. Thus sols that have been arced for only a few minutes contain practically as much gold after centrifuging six hours as after thirty minutes. Let us further assume that as the arcing process is continued part of these gold atoms evaporating from the electrodes strike gold particles, previously formed and at that moment located in the wall of the sol surrounding the electrodes. That they will build up on and not be reflected is highly probable.[5] Thus as the arcing process proceeds these particles continue to grow. At the same time new particles are continually being formed. These assumptions explain, we believe, these curves. Thus

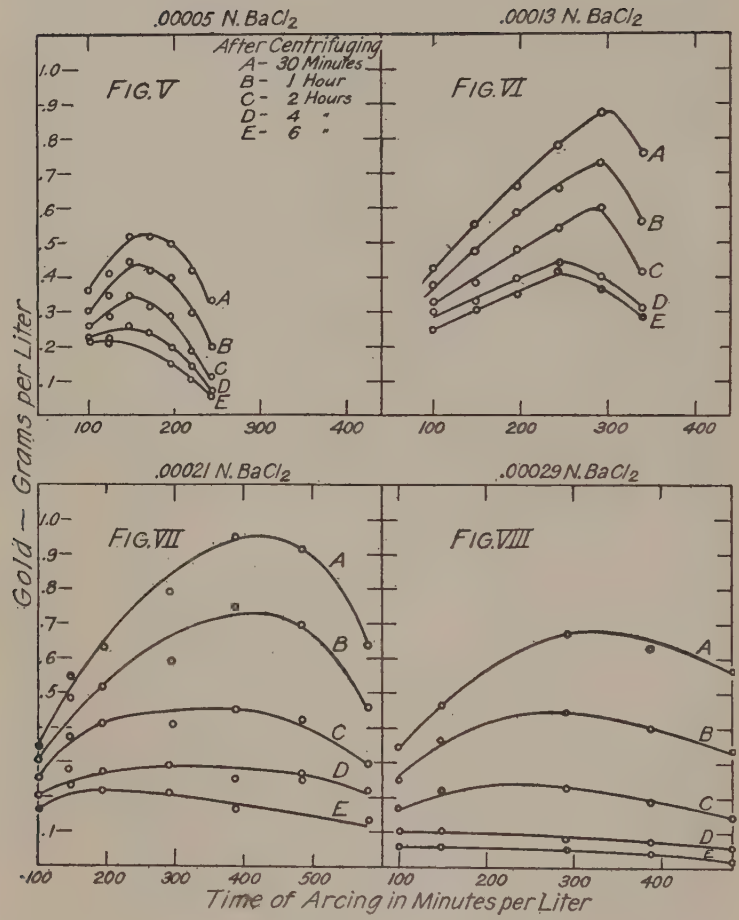
in Curve B, Fig. I, it is found that the total amount of gold has been increased by the continued arcing beyond that in Curve A. Also it seems evident that the size of some of the particles has been increased as shown by the fact that they are more rapidly thrown out by centrifuging. In Curve C of Fig. I it is found that a still greater total amount of gold, than that in Curve B, is present. Thus it seems evident that a further increase in the sizes of the particles has been made, for they are more rapidly thrown out by centrifuging than before. Further the number of small particles has been increased as shown by the fact that a greater quantity of gold is stable after centrifuging six hours.

It is impossible to say, at the present time, what is the exact nature of the part played by the electrolyte. However, the hypothesis advanced by Beans and Eastlack[2] is, that the particles of a Bredig gold sol consist essentially of a "complex" between the gold particles and the ions of an electrolyte, the presence of which is necessary to the stability of the sol. Certainly the presence of the ions is essential in the formation of the nuclei. Thus in a solution containing a given concentration of ions there is material for the formation of a definite number of nuclei or centers for the formation of the gold particles. Since a particle may begin to grow the next instant after it is formed, it would be very difficult to separate the two processes. Since the possible number of nuclei which may be formed for a definite concentration of electrolyte is limited, there comes a time, with continued arcing, when they are all formed. These, however, continue to grow and thus the total weight of these small particles (the quantity of gold left in the sol after six hours of centrifuging) must continuously decrease. This is shown in Curves D, E, F, and G of Fig. I.

Due to the fact that an error of high percentage is introduced in determinations of less than thirty minutes because of the time necessary for starting and stopping the centrifuge, these curves could not be continued closer to the gold axis. Nevertheless, it is safe to state that the curves A, B, C, D, etc., would cut the gold axis at points successively

higher and higher, thus demonstrating the fact that as more and more gold goes into this colloidal form, more and more of these particles have become so large in size that they are quickly thrown out by the centrifuge. That this is true is shown more conclusively in Figures II, III and IV. In Fig. II it is seen that with a concentration of electrolyte higher than that shown in Fig. I, there is possible the formation of a large number of nuclei. This is shown by the fact that the amount of gold remaining in solution after six hours of centrifuging, as shown in Curve D of Fig. II, is higher than that of Curve C in Fig. I. The curves of Figures II, III and IV are analogous to those of Fig. I and the same conclusions may be drawn. However, in Fig. III, although the concentration of barium chloride is greater than in Fig. II, apparently the maximum number of nuclei which can be formed is decreased. The stabilizing effect of the chloride ion has been mentioned. These gold particles, stabilized by the formation of a complex with the negative ion acquire a negative charge. That these particles, in brownian movement do not combine under ordinary circumstances has been ascribed to the fact that they are all similarly charged and repulse each other.

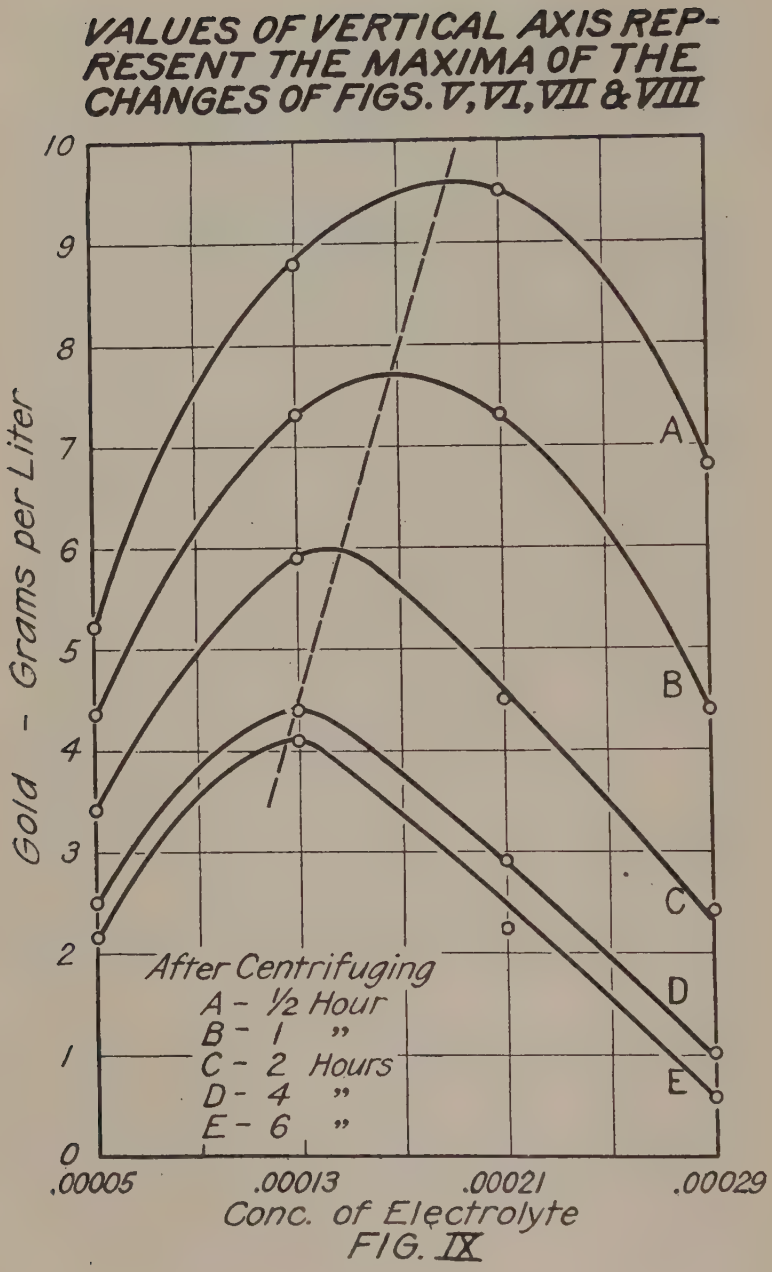
However the influence of the barium ion cannot be neglected. If an excess of electrolyte is added to a stable sol it will be precipitated out. Kruyt and Van der Spek show that these particles have a surface potential which is lowered by the addition of the electrolyte. It is not necessary, however, to reduce this surface potential to zero but to a value called the critical potential at which the sol begins to precipitate out. In the light of this theory, Fig. III shows that, when these particles are produced in the presence of an excess of the electrolyte, the surface potential is low enough that the small particles combine with each other forming larger particles, and particles more readily thrown out by the centrifuge. Thus part of the electrolyte is used up and the number of particles which is formed apparently is less than for a slightly smaller concentration. In Fig. IV with .00029 N barium chloride this condition is even


.00005 N. BaCl2
.00013 N. BaCl2
After Centrifuging
A- 30 Minutes
B- 1 Hour
C- 2 Hours
D- 4 "
E- 6 "
FIG. V
FIG. VI
.00021 N. BaCl2
.00029 N. BaCl2
FIG. VII
FIG. VIII
Gold — Grams per Liter
Time of Arcing in Minutes per Liter

more marked. More will be said of this phenomenon in connection with Figures V, VI, VII and VIII.

Again in Figures I, II, III and IV, it is seen that for a given concentration of electrolyte and after a given length of time of centrifuging the amount of gold which remains in the sol increases with increasing time of arcing, passes through a maximum, and falls. This is shown directly in Figures V, VI, VII and VIII. These curves show the relationship between time of arcing and the amount of colloidal gold remaining in stable form after centrifuging for different lengths of time. They show that these sols contain particles of all sizes from the coarse suspended material to the finely divided particles of only a few gold atoms. The coarse particles are quickly thrown out, while the smaller and smaller particles are thrown out only after longer periods of centrifuging. However, this change is gradual and continuous, so that it is impossible to choose any one time of centrifuging and say that the particles thrown out are all large, coarse particles and those remaining are small, colloidal particles. These curves show the uselessness of estimating the size of such colloidal particles. Clearly the particles are of many sizes. Also calculations of the average charge on a particle, in which values, supposed to represent the average size of particles, are used, are without significance. If in a given sol a large number of the particles were close in size to a given value it would be possible to find and make use of such an average. However, such is not the case. The particles vary in size uniformly from very small to large particles as shown by the form of the curves in Figures I, II, III and IV.

A great many attempts have been made to arrive at a relationship between a size of particle and the color of the sol 12, 13, 14. While chemical methods are described for the preparation of red, blue, brown, violet and black gold sols, it is by no means certain that sols so prepared consist of simple gold particles nor that the variation in color relates in any essential way to the difference in size of the particles. As a direct result of the author's work it seems


VALUES OF VERTICAL AXIS REPRESENT THE MAXIMA OF THE CHANGES OF FIGS. V, VI, VII & VIII
Gold - Grams per Liter
10
9
8
7
6
5
4
3
2
1
0
A
B
C
D
E
After Centrifuging
A - ½ Hour
B - 1 "
C - 2 Hours
D - 4 "
E - 6 "
.00005
.00013
.00021
.00029
Conc. of Electrolyte
FIG. IX

certain that gold sols prepared by the Bredig method contain particles of the most varied sizes. These stable sols are uniformly red (the depth of color depending upon the concentration of gold). Throughout the range of centrifuging shown in Figures I, II, III and IV, no change in color was produced, yet a fractional separation according to size has certainly been made.

It is also seen that, although a given time of arcing may give the maximum quantity of stable colloidal gold for a given time of centrifuging, it does not do so for another. Thus if the centrifuge is to be used to separate certain large particles from the smaller, in order to obtain reproducible and comparable results, the same length of time of centrifuging must be used. These curves are further evidence supporting the assumption that the smallest particles form first and that these increase in size with increased time of arcing. If the assumption is correct, the maximum for the larger particles could not occur at the same time of arcing as that for the smallest particles, but would occur somewhat later. Further, this difference between the times of arcing at which these maxima occur will be increasingly greater with increased concentrations. This is shown conclusively by Figures V, VI, VII and VIII. Thus the statement of Miller that, with increasing time of arcing, the amount of gold in the sol passes through a maximum value, is quantitatively demonstrated to be true.

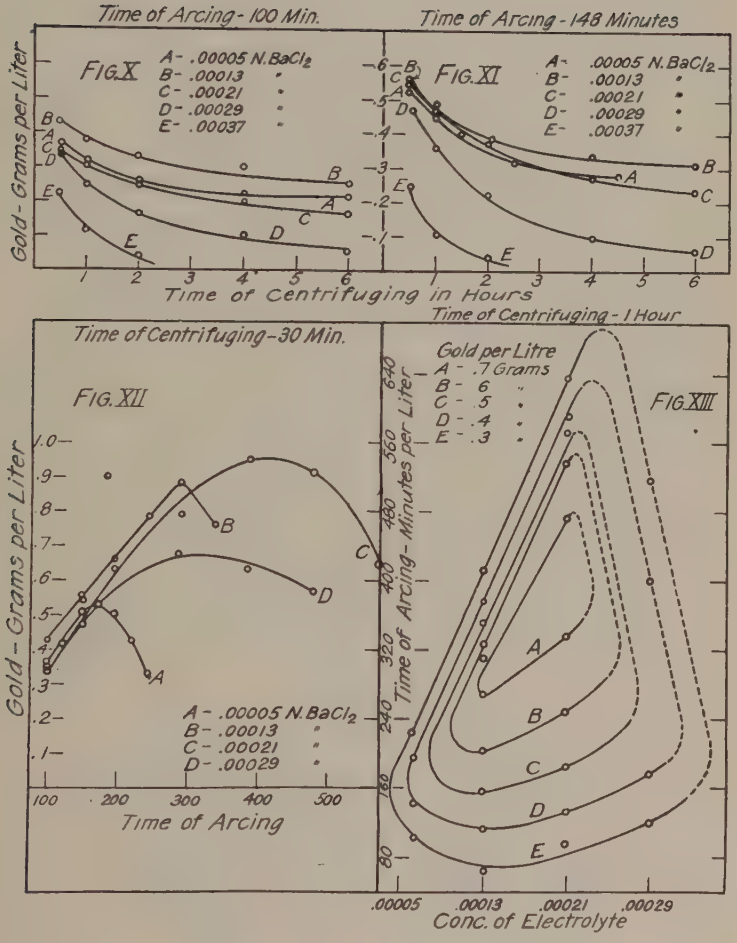
It may be noticed, too, that the quantities of gold that may be obtained in sols stabilized by barium chloride are smaller than those obtained by Miller, who used only electrolytes giving monovalent ions. Kruyt and Van der Spek[9] have demonstrated the relative flocculating powers of the mono-, di-, and trivalent ions. Thus it would appear that, due to this greater precipitating power of the barium ion, the chloride ion is only able to stabilize smaller quantities of the gold in its presence.

The exact nature of these two forces, i. e., the stabilizing and the coagulating effects, is not at present known. Ac-

cording to the best evidences colloidal gold is stabilized by a kind of combination between the chloride ion and the gold. According to Kautsky and Pauli[7] under favorable circumstances one chloride ion may hold as many as 1400 gold atoms. This is the co-called "complex." It is a union strong enough to resist centrifuging and not strong enough to resist freezing.[3] On the other hand, positive ions are supposed to exert a precipitating influence, in particular the evidence shows the divalent ions to be very strong precipitating agents.[8] This explanation is satisfactory if we look only at the left half of such curves as those of Fig. V. Why should the slope of the curves in the right half become negative? Kruyt and Van der Spek[8] state that as one adds an electrolyte to a stable sol, the charge of the particles concerned is lowered (surface potantial is decreased) and on that account the work of repulsion, which the particles exerted upon one another is annulled; the surface tension increases and promotes flocculation. This explanation serves very well to explain the coagulation or precipitation of a stable sol by the addition of an electrolyte. However, this case is somewhat different. The electrolyte has not been added to a stable sol. An excess of it was present as the sol was being made. The ratio of the concentrations of the chloride ion in the sol to that of the barium ion has not been changed. Hence it would seem that a greater concentration of electrolyte should stabilize a large amount of gold, unless the surface potential (or other property) passes through a minimum (or maximum) with the addition of electrolyte. No work has been found indicating that this takes place.

Part of the chloride ions are bound within the complex. They have given their charges to these particles. According to Powis[11] this charge or surface potential must be lowered before precipitation may be brought about.

The addition of an electrolyte serves this purpose. Svedberg in an investigation of brownian movement has shown that the velocity of the particles is changed only secondarily by the addition of electrolyte.[10] This addition causes coagu-


Time of Arcing - 100 Min.
FIG. X
A - .00005 N. BaCl2
B - .00013 "
C - .00021 "
D - .00029 "
E - .00037 "
Gold - Grams per Liter
Time of Arcing - 148 Minutes
FIG. XI
Time of Centrifuging in Hours
Time of Centrifuging - 30 Min.
FIG. XII
Gold - Grams per Liter
Time of Arcing
Time of Centrifuging - 1 Hour
Gold per Litre
A - .7 Grams
B - .6 "
C - .5 "
D - .4 "
E - .3 "
FIG. XIII
Time of Arcing - Minutes per Liter
Conc. of Electrolyte
.00005
.00013
.00021
.00029

lation or particle growth. Again he was dealing with electrolyte added to stable sols. In the case of these gold sols formed in the presence of an excess of electrolyte the best explanation seems to be that part of the electrolyte furnishes the stabilizing ions and that the remainder exerts the influence which causes this "coagulation or particle growth." Thus the excess electrolyte is used up in the rapid formation of larger particles by coagulation. These particles are more quickly thrown out by the centrifuge and a smaller quantity of gold remains. That this is true is shown in Figures X and XI. In Fig. X are shown curves representing solutions, all of which were arced 100 minutes per liter. All conditions were the same except the concentration of electrolyte. Thus it is shown that a sol prepared in .00013 N barium chloride (Curve B, Fig. X) by arcing for 100 minutes per liter contains more stable gold sol after centrifuging than one made in a solution of .00005 N barium chloride. However, with greater concentrations than .00013 N barium chloride less and less of the stable gold (Curves C, D and E) remains after centrifuging. Thus the presence of the excess electrolyte has caused these small nuclei to combine with each other leaving fewer of the smallest particles and a larger proportion of the larger particles even though the treatment, such as time of arcing, etc., was in every case the same. Fig. XI shows more markedly the difference between these sols after a longer period of arcing. These curves show that, for a given length of time of arcing, the amount of stable gold, remaining after centrifuging a given length of time, varies, passing from zero, for zero concentration of barium chloride, through a maximum value at approximately .00013 N barium chloride and falling again to zero between .00030 N and .00040 N, depending upon the length of time of centrifuging. Thus the greatest amount of stable gold is obtained with a concentration near .00013 N, when barium chloride is used as the stabilizing electrolyte.

In comparing Figures V, VI, VII and VIII it will be noticed that there is an optimum concentration of elec-

trolyte in which to arc in order to obtain the highest possible maximum. Fig. IX shows the maximum point of each of these curves plotted against the concentration of electrolyte in which it was obtained. Thus Curve A represents the four maxima of the A curves in Figures V, VI, VII and VIII, respectively, etc. The differences in the times of arcing necessary to obtain these maxima have been neglected. Thus it is shown that the optimum concentration of electrolyte for obtaining the maximum quantity of colloidal gold varies with the treatment of the sols in the centrifuge. The concentration of electrolyte which yields the greatest number of the smallest gold particles (those remaining after six hours' centrifuging) is markedly smaller than that which yields the greatest possible number of the largest particles.

In Fig. XII the A curves of Figures V, VI, VII and VIII, respectively, are brought together. These curves show, relatively, the lengths of time required to obtain various concentrations of gold in the presence of the different concentrations of barium chloride. In order to make the contrast as great as possible the curves obtained for a short time of centrifuging (30 minutes) were used. Similar figures may be obtained for each time of centrifuging. If these curves (A, B, C, D of Fig. XII) are considered as projections from a space figure whose third dimension is concentration of electrolyte, the space figure may be readily visualized and the significance of Fig. XIII will be more readily understood.

Fig. XIII is a contour map of a similar space model, (i. e., of the space figure obtained by considering the time of centrifuging constant at one hour) using the time of arcing, concentration of electrolyte and concentration of stable gold as the three axes. Practically, Fig. XIII, shows the various conditions under which it is possible to arrive at sols of the same concentration of colloidal gold. Thus if one arcs in a .00013 N solution of barium chloride for approximately 72 minutes per liter of solution and then centrifuges for one hour, the concentration of gold will be .3 gram per liter. If he had continued the arcing for approximately 410 minutes

and centrifuged the same length of time the concentration of electrolyte will again be .3 gram per liter. Or if one arcs either 96 minutes or 690 minutes in a solution of .00024 N $BaCl_2$ and again centrifuge one hour the concentration of gold will be the same, .3 gram per liter. Thus it is possible to have many solutions of colloidal gold with identical concentrations yet with widely varying properties. One may contain a larger number of smaller particles and another, produced under different conditions, may contain a smaller number of larger particles, making the total weight of gold in the sol the same. Thus it is not enough to know the concentration of gold per liter in making a study of the colloidal properties of these solutions. The exact conditions under which the solutions were produced must be known before a comparison of their properties may be made.

Miller has diluted and centrifuged a stable gold sol of known gold concentration and found that the stability of the particles has not changed. This is now easily explained. It has been shown that there is for each concentration of electrolyte a maximum number of these particles which can be formed. After they are formed, however, mere dilution of the sol makes no change which can cause a change in the stability of these particles.

To be certain that the relative time of stirring had no effect on the size of the particles, a sol was made by arcing twenty-five minutes in .00005 N barium chloride. This sol was then stirred for twelve hours at the same rate, and samples taken every three hours. These samples were immediately centrifuged one hour and thirty minutes each. Upon analysis twenty-five cc of the original solution Sample No. 1 was found to contain 6.7 milligrams of gold. At the end of three hours stirring Sample No. 2 contained 6.4 milligrams; No. 3 (6 hours), 6.5 milligrams; No. 4 (9 hours), 6.6 milligrams, and No. 5 (12 hours), 6.7 milligrams of gold. Within experimental error, these values may be regarded as constant. Hence merely stirring these sols produces no change in their stability.

SUMMARY

1. The arcing stand has been improved, making it possible to obtain a continuous arc.

2. The factors influencing particle formation and growth, by the Bredig method, have been discovered. Four of these factors have been chosen for study and were treated as variables; the remainder was held constant.

3. The relationship between the amount of stable gold and time of arcing has been studied. A theory of gold particle growth by condensation (distinguished from coagulation) has been advanced.

4. The relationship between the amount of stable gold and time of centrifuging has been studied. It has been shown that Bredig gold sols consist of particles having a uniform variation in size between extreme limits. In view of this, calculation of "average size of particles or charge of particles" are without significance.

5. The relationship between stable gold and concentration of electrolyte has been studied. It is found that these maximum values depend upon the treatment of the sols in the centrifuge.

6. The influence of an excess of electrolyte upon particle growth during arcing has been shown.

7. A series of space figures (a contour map representing these figures is shown in Fig. XIII), showing the relationships between concentration of gold, concentration of electrolyte, time of arcing, and time of centrifuging, has been obtained.

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